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## (54) POLYMERIZATION OF ALPHA-OLEFINS

(71) We, MONTECATINI EDISON S.p.A., a Body Corporate organised and existing under the laws of Italy, of 31 Foro Buonapart, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the selective polymerization of alpha-olefins to predominantly isotactic or predominantly atactic polymers.

The invention provides a process for the preparation of a polymer which comprises homopolymerizing an alpha-mono-olefin in the presence of a catalyst comprising a reaction product of a hydride or organo-metallic compound of a metal of Group I, II or III of the Periodic System with a titanium compound supported on a carrier comprising an activated anhydrous halide of magnesium or manganese. By this process it is possible to obtain polymers in a yield so high that it is not necessary to purify them by removal of catalyst residues. By alpha-mono-olefin we mean a compound of the formula  $\text{CH}_2=\text{CHR}$ , wherein R is an alkyl radical, preferably containing from 1 to 6 carbon atoms such as propylene, butene - 1, pentene - 1, hexene - 1, 4 - methyl - pentene - 1, or 3 - methyl - butene - 1. The Periodic System referred to herein is that of Mendeleef.

The formation of predominantly isotactic polymers is promoted by polymerization of the monomer dissolved in an inert liquid diluent; or by the use of a catalyst modified by an electron-donor compound, in which the electron-donor atom is N, O, P or S. The formation of predominantly atactic polymers is favoured by high monomer concentrations, by operating for instance with the liquid monomer in the absence of any inert diluent, or in the presence of such diluent in a limited

quantity, lower as a rule than 50% by weight with respect to the monomer.

The halide of magnesium or manganese is preferably activated to the extent that in its X-ray spectrum at least the most intense diffraction line in the spectrum of the non-activated halide is decreased in intensity and in its place there is a broadened halo, and/or it has a surface area greater than 3 sq. m. per g. For instance, in the case of the anhydrous magnesium chloride, some very active forms have in the X-ray spectrum the reflection at  $d=2.56 \text{ \AA}$  (which is the most intense of the spectrum of normal magnesium chloride) is of lower intensity and there is a broadened halo in its place. Similarly for some active forms of manganese chloride, the reflection intensity at  $d=2.57 \text{ \AA}$  (the most intense in the spectrum of normal manganese chloride) is of lower intensity and in its place there is a broadened halo. The most active forms have a surface area greater than 15 sq. m. per g.

The activated magnesium or manganese halide may be prepared before or during contact with the titanium compound. One of the most suitable methods comprises dissolving the halide in an alcohol, ester or other organic solvent, removing the majority of the solvent by a fast evaporation and completing the removal under reduced pressure and at a temperature in general above  $100^\circ\text{C}$ , preferably from  $150^\circ$  to  $500^\circ\text{C}$ . Activated forms of the halides may alternatively be obtained by very fine grinding or by another other physical method in which the carrier particles are subjected to frictional and/or shearing forces.

The preferred method of activation, and at the same time for the preparation of the supported catalyst component comprises dispersing the titanium compound in the halide by grinding them together. The grinding is preferably carried out in a ball mill, by working

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in the dry state, in the absence of any inert diluent. Besides grinding, the preparation of the supported catalyst component may be achieved by simply mixing together the titanium compound with previously ground magnesium or manganese halides.

The catalyst may have the composition and/or be modified as in our Patent Specifications 1,277,349, 1,286,867, 1,289,462, 1,291,552, 1,292,853, 1,299,532, 1,314,053, 1,305,610, 1,310,547, and others. For example anhydrous compounds of elements of Groups I, II, III or IV of the Periodic System may be added during the preparation of the carrier without substantially reducing the activity of the catalyst but reducing, and even eliminating, the harmful corrosion action due to the presence of the halide in subsequent moulding or forming of the polymer itself. Typical examples of such compounds are those of the formulae:  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{NaBr}$ ,  $\text{BeCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{ZnI}_2$ ,  $\text{CdCl}_2$ ,  $\text{CdBr}_2$ ,  $\text{Cu}_2\text{Cl}_2$ ,  $\text{HgCl}_2$ ,  $\text{PbCl}_2$ ,  $\text{SnCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{CrO}_4$ ,  $\text{Na}_2\text{B}_4\text{O}_7$ ,  $\text{ZnO}$ ,  $\text{BeO}$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{CaSO}_4$ ,  $\text{CaCO}_3$ ,  $\text{BeSO}_4$ ,  $\text{Ca}(\text{C}_17\text{H}_{35}\text{COO})_2$ ,  $\text{CH}_2=\text{CH}-\text{SO}_3\text{Na}$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Al}_2(\text{SO}_4)_3$ . The quantities of these compounds that may be incorporated into the anhydrous magnesium or manganese halide without appreciably altering the activity of the catalyst vary within a wide range. Mixtures capable of providing catalysts having activities substantially equal to those obtained from carriers consisting only of activated anhydrous magnesium or manganese halide, may contain quantities of these compounds from 1 to 80%, preferably from 30% to 70% by weight.

Titanium compounds that are suitable for the preparation of catalysts according to the invention include alcoholates, halides, oxyhalides, haloalcoholates, ammonium, alkylammonium or alkali metal halotitanates or halotitanites, amides, haloamides, and salts of organic acids. These compounds may be combined with alcoholates and amides of alkali metals, to give useful catalysts such as those of the formulae:  $\text{LiTi}(\text{OC}_2\text{H}_5)_2\text{Cl}_2$  and  $\text{LiTi}(\text{C}_6\text{H}_5\text{N})_4$  ( $\text{C}_6\text{H}_5\text{N}$  indicates a carboxyl radical). Typical examples of suitable titanium compounds are those of the formulae:

$\text{TiCl}_3$ ,  $\text{TiCl}_4$ ,  $3\text{TiCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{TiI}_4$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl}$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)_2\text{Cl}_2$ ,  $\text{Ti}[\text{O}-\text{C}(\text{CH}_3)=\text{CH}-\text{CO}-\text{CH}_3]_2\text{Cl}_2$ ,  $\text{Ti}[\text{N}(\text{C}_6\text{H}_5)_2]_3\text{Cl}_3$ ,  $\text{Ti}[\text{N}(\text{C}_6\text{H}_5)_2]_2\text{Cl}_4$ ,  $\text{Ti}[\text{N}(\text{C}_6\text{H}_5)_2]_3$ ,  $\text{TiCl}_3-\text{OSO}_2-\text{C}_6\text{H}_5$ ,  $\text{Ti}(\text{C}_6\text{H}_5\text{COO})\text{Cl}$ ,  $[\text{N}(\text{C}_6\text{H}_5)_2]_2\text{TiCl}_2$ ,  $[\text{N}(\text{CH}_3)_2]_2\text{TiCl}_2$ ,  $\text{TiBr}_2\text{O}(\text{C}_6\text{H}_5)_2$ ,  $2\text{TiCl}_3\text{C}_6\text{H}_5\text{N}$ ,  $\text{LiTi}(\text{OC}_2\text{H}_5)_2\text{Cl}_2$ , and  $\text{LiTi}(\text{C}_6\text{H}_5\text{N})_4$  (lithium-titanium tetracarbazyl). The quantity of titanium compound usable for the preparation of the supported catalyst component may be from 0.01% to above 30% by weight with respect to the car-

rier. Particularly interesting results, as far as the yield in polymer is concerned, with reference both to the titanium compound and to the carrier itself, are obtained with from 1% to 10% by weight of titanium compound on the carrier.

Hydrides and metalorganic compounds particularly suitable for use in the preparation of the catalyst include those of the formulae:

$\text{Al}(\text{C}_2\text{H}_5)_3$ ,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ ,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Br}$ ,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{I}$ ,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ ,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Br}$ ,  $\text{LiAl}(\text{C}_2\text{H}_5)_4$ ,  $\text{LiC}_4\text{H}_9$ . The molar ratio between the hydride or organometallic compound and the titanium compound is not critical but is preferably from 50 to 1000.

Unexpectedly, it has been found that the catalysts of the invention which promote the formation of prevailingly isotactic polymers are derived from tetravalent titanium compounds (in particular titanium tetrachloride) and not from the trivalent titanium compounds which surprisingly promote the formation of predominantly atactic polymers. The use of solid diluent compounds of metals of Groups I or II of the Periodic System in addition to the support in the preparation of the catalyst, tends to facilitate the formation of isotactic polymers. The use of diluent compounds of elements of Groups III and IV of the Periodic System tends to lower the formation of these polymers. For instance, potassium or lithium chloride tends to increase the quantity of isotactic polymer produced; silica tends to lower it.

Catalysts for the preparation of the prevailingly isotactic polymers may be obtained by reacting a supported catalyst component with an electron-donor compound dissolved in a solvent. Another method comprises grinding together the titanium compound and the carrier in the presence of the electron-donor compound. It is however possible first to treat the titanium compound with the electron-donor compound so as to obtain an addition compound, and then to contact the addition compound with the carrier. The molar ratio between titanium and the electron-donor atom in the addition compounds is generally from 1:1 and 1:6. When the treatment with the electron-donor compound is carried out in the presence of the carrier, the quantity of the electron-donor compound should be such as will ensure an atomic ratio titanium:electron-donor from 1:0.2 to 1:20, preferably from 1:1 to 1:6. Examples of suitable electron-donor compounds are ethers, thioethers, amines, phosphines, ketones, and esters. Particularly interesting results have been obtained with  $\text{N,N',N'',N'''} - \text{tetramethyl} - \text{ethylene-diamine}$ ,  $\text{dimethoxyethane}$ ,  $\text{diethyleneglycol-dimethyl-ether}$ ,  $\text{tetrahydrofuran}$ , and  $\text{dioxan}$ .

The inert liquid diluents usable in the process of the invention include aliphatic, aromatic and cycloaliphatic hydrocarbons, for

example *n* - hexane, *n* - heptane, cyclohexane, benzene, and toluene. The polymerization may be conducted at from  $-80^{\circ}\text{C}$  to  $+200^{\circ}\text{C}$ , preferably from  $0^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ . Preferably one operates at an alpha-olefin partial pressure greater than atmospheric pressure. Regulation of the molecular weight of the polymer during the polymerization can be carried out by operating in the presence of an alkyl halide, organometallic zinc or cadmium compound or hydrogen, for example.

The invention is illustrated by the following Examples in which, where not otherwise indicated, the percentages are by weight; the inherent viscosity of the polymer was measured in tetralin at  $135^{\circ}\text{C}$  at a concentration of 0.25 g of polymer in 100 cc of solvent.

#### EXAMPLE 1

8.17 g of anhydrous magnesium chloride and 0.41 g of titanium tetrachloride were ground together under a nitrogen atmosphere for 16 hours, in a glass mill (100 mm long, 50 mm diameter) containing 550 g of steel balls of 9.5 mm individual diameter. The ground product shows under X-ray examination a broadening of the diffraction lines, and has a surface area of 22 sq. m. per g. 0.244 g of the ground product (having a titanium content of 1.20%), 1.6 g (2 cc) of aluminium triisobutyl and 50 cc of anhydrous *n* - heptane, were injected under nitrogen pressure into a 3 litre stainless steel autoclave maintained at  $25^{\circ}\text{C}$ . This autoclave was fitted with a magnetic stirrer and contained 640 g of anhydrous propylene. After 4—5 hours, the stirring was interrupted, the unpolymerized propylene was discharged, and from the autoclave there was unloaded a translucent, white and compact mass. After drying, this mass weighed 540 g which correspond to a yield, with respect to the titanium used, of 183,500 g per g. The inherent viscosity in tetralin at  $135^{\circ}\text{C}$  was 1.6 dl/g. The crystallinity under X-ray examination was 29%. Extraction with boiling solvents gave: diethyl ether extract=52.5%; *n* - heptane extract=26.5%; heptane residue=21%.

#### EXAMPLE 2

Example 1 was repeated but using 0.415 g of the supported catalyst and as organometallic compound of 2 g of aluminium diethyl mono-chloride polymerization was carried on for 8 hours at  $65^{\circ}\text{C}$ . There were obtained 440 g of a polymer similar in appearance to that of Example 1 in a yield corresponding to 88,000 g per g of titanium used. The inherent viscosity was 1.2 dl/g, and the crystallinity 28%. Extraction with boiling solvents gave a diethyl ether extract of 53.5%, an *n* - heptane extract of 23.7% and a heptane residue of 22.8%.

#### EXAMPLE 3

0.38 g of anhydrous magnesium chloride, 3 g of anhydrous lithium chloride and 0.41 g of titanium tetrachloride were ground together under a nitrogen atmosphere for 16 hours as in Example 1. The ground product showed a broadening of the diffraction lines in the X-ray spectrum and a surface area of 25 sq. m per g. 0.3834 g of the product ground (having a titanium content of 1.06%) were suspended in 10 cc of anhydrous *n* - heptane and were mixed with 0.064 g of  $\text{N,N',N'',N'''} - \text{tetramethylethylenediamine}$ . The mixture was left for 45 minutes under stirring at room temperature. It was diluted with 300 cc of *n* - heptane, 1 cc of aluminium triethyl was added, and the resulting suspension was introduced, under a nitrogen atmosphere into a 1 litre stainless steel rocking autoclave. Propylene was introduced to build up a pressure of 4 atmospheres absolute which, together with the temperature, was maintained constant (by continuously feeding the monomer) throughout the test. After 5 hours the polymerization was interrupted and, after coagulation with a methanol/acetone (1:1) mixture, filtering and drying, 47 g of polymer having an inherent viscosity of 2.4 dl/g was separated. Successive extraction with boiling solvents yielded: diethyl ether extract=23%, *n*-heptane extract=8%, heptane residue=69%.

Using 0.44 g of the same catalyst, but omitting the reaction with the amine, there were obtained 111 g of a polymer having an inherent viscosity of 1.2 dl/g. The extraction with boiling solvents yielded: diethyl ether extract=33%, heptane extract=22.5%, heptane residue=44.5%.

#### EXAMPLE 4

9.60 g of anhydrous magnesium chloride, 0.41 g of titanium tetrachloride were ground together for 88 hours under the same conditions as in Example 1. The product showed a broadening of all diffraction lines in the X-ray spectrum. 0.4203 g of the product were made to react, under stirring and at room temperature, for 45 minutes with 0.070 g of  $\text{N,N',N'',N'''} - \text{tetramethylethylenediamine}$  in the presence of 10 cc of *n*-heptane. The mixture was diluted with 300 cc of *n*-heptane, mixed with 1 cc of aluminium triethyl, and then propylene was polymerized therewith under the same conditions as in Example 3. There were obtained 63 g of a polymer having an inherent viscosity of 2.2 dl/g. Extraction with boiling solvents gave the following results: diethyl ether extract=22.5%, heptane extract=12.5%, heptane residue=65%.

#### EXAMPLE 5

1251 g of anhydrous magnesium chloride and 1.3 g of a compound of the formula

$\text{TiCl}_4[\text{N}(\text{C}_2\text{H}_5)_2]_2$  were ground together for 36 hours for activation as in Example 1. 0.330 g of the product thus obtained (having a titanium content of 0.99%), 2 cc of aluminium tri-isobutyl and 50 cc of *n*-heptane were introduced into a 3 litre stainless steel autoclave provided with a magnetic stirrer. Immediately after, there were introduced 1000 g of propylene and the whole mixture was kept at a constant temperature (30°C) throughout the test. After 8 hours the polymerization was interrupted and, as in Example 1, there were separated 550 g of polymer: a yield of 170,000 g per g of titanium used. The inherent viscosity was 1.58 dl/g. Extraction with boiling solvents gave the following results: diethyl ether extract=56%, heptane extract=22.7%, heptane residue=21.3%.

#### EXAMPLE 6

1.701 g of anhydrous magnesium chloride, 1.6240 g of silica (Syloid (Registered Trade Mark) Al 1 Grace-Davidson) calcined at 900°C, and 0.140 g of titanium tetrachloride were ground together for 16 hours for activation as in Example 1. 0.195 g of the mixture thus produced (having a titanium content of 1.02%) were used for the polymerization of propylene as in Example 5 except that the polymerization time was 7.5 hours. There were obtained 310 g of polymer, corresponding to a yield of 156,000 g per g of titanium used. The inherent viscosity was 1.16 dl/g. Extraction with boiling solvents gave: diethyl ether extract=62.6%, *n*-heptane extract=25.6%, heptane residue=11.8%.

#### EXAMPLE 7

0.112 g of the catalyst in Example 6 were introduced together with 1 cc of aluminium tri-isobutyl, 15 cc of *n*-heptane, into a 500 cc glass autoclave provided with an anchor stirrer and containing 300 cc of hexene-1. Polymerization was conducted for 4 hours at 30°C, and then for a further 4 hours at 65°C. After evaporating off the unreacted monomer and the solvent, there were obtained 92.3 g of a white rubbery polymer whose inherent viscosity was 3.88 dl/g. The yield in polymer was 81,000 g per g of titanium used. The polymer was completely soluble in diethyl ether.

#### EXAMPLE 8

10.81 g of anhydrous magnesium chloride and 0.45 g of titanium trichloride propoxide ( $\text{TiCl}_3\text{OC}_2\text{H}_5$ ) were ground together for 16 hours as for activation in Example 1. 0.8822 g of the product thus obtained (having a titanium content of 0.9%) were used for the polymerization of propylene as in Example 5. There were obtained 175 g of polypropylene, which corresponds to a yield of 85,000 g per g of titanium used. The inherent viscosity was 1.55 dl/g. Extraction with boil-

ing solvents gave: diethyl ether extract=52%, *n*-heptane extract=29.7%, heptane residue=18.3%.

#### EXAMPLE 9

5.99 g of anhydrous magnesium chloride, 3.66 g of anhydrous sodium chloride and 0.41 g of titanium tetrachloride were ground together for 24 hours for activation under a nitrogen atmosphere as in Example 1. 0.1426 g of the mixture thus obtained (having a titanium content of 0.995%) were used for the polymerization of propylene as in Example 5. There were obtained 150 g of polymer, a yield of 105,000 g per g of titanium used. The inherent viscosity was 1.49 dl/g. Extraction with boiling solvents gave: diethyl ether extract=52.5%, *n*-heptane extract=31.9%, heptane residue=15.8%.

#### EXAMPLE 10

The procedure of Example 6 was followed using 0.2107 g of supported catalyst and adding 2 atmospheres of hydrogen to regulate the molecular weight of the polymer. After 8 hours the polymerization was interrupted, and from the reaction mass 240 g of polymer were separated: a yield of 110,000 g of polymer per g of titanium used. The inherent viscosity was 0.25 dl/g. Extraction with boiling solvents gave: diethyl ether extract=64.6%; *n*-heptane extract=23.8%, heptane residue=11.6%.

#### EXAMPLE 11

11.3885 g of anhydrous magnesium chloride and 0.2608 g of a complex of the formula  $3\text{TiCl}_4\cdot\text{AlCl}_3$  (obtained by reduction of titanium tetrachloride with metallic aluminium and activated by grinding), were ground together under a nitrogen atmosphere for 16 hours for activation as in Example 1. 0.3596 g of the mixture thus obtained (having a titanium content of 0.52%) were used for the polymerization of propylene as in Example 5. There were obtained 310 g of polymer: a yield of 165,000 g per g of titanium used. The inherent viscosity was 1.58 dl/g. Extraction with boiling solvents gave: diethyl ether extract=52%, *n*-heptane extract=32.5%, heptane residue=15.5%.

#### EXAMPLE 12

30 g of anhydrous manganese chloride were dissolved in 100 cc of anhydrous ethanol. By fast evaporation of the alcohol and by a subsequent drying at 3000°C, under a pressure of 0.5 mmHg, there was obtained a powder which had a specific surface area of 22 sq. cm/g. 11.393 g of the manganese chloride thus prepared and 0.45 g of titanium tetrachloride were ground together for 44 hours as in Example 1. 0.2110 g of the product (having a titanium content of 0.96%) were used for the polymerization of propylene as in

Example 5. There were obtained 150 g of polymer: a yield of 70,000 g per g of titanium used. The inherent viscosity was 1.33 dl/g. Extraction with boiling solvents gave:  
 5 diethyl ether extract=57%, *n*-heptane extract=22%, heptane residue=21%.

# WHAT WE CLAIM IS:—

1. A process for the preparation of a polymer which comprises homopolymerizing an  
 10 alpha-mono-olefin as herein defined in the presence of a catalyst comprising a reaction product of a hydride or organometallic compound of a metal of Group I, II or III of  
 15 the Periodic System with a titanium compound supported on a carrier comprising an activated anhydrous halide of magnesium or manganese.

2. A process according to claim 1 in which the alpha-mono-olefin is propylene, butene-  
 20 1, pentene - 1, hexene - 1, 4 - methylpentene - 1, or 3 - methyl - butene - 1.

3. A process according to claim 1 or claim 2 in which the activated halide has in its X-ray spectrum the most intense diffraction  
 25 line in the spectrum of the non-activated halide decreased in intensity and replaced by a broadened halo.

4. A process according to any of the preceding claims in which the activated halide  
 30 has a surface area greater than 15 sq. m per g.

5. A process according to any of the preceding claims in which the catalyst is modified by an electron-donor compound in which  
 35 the electron donor atom is N, O, P or S.

6. A process according to any of claims 1 to 4 in which the polymerization is carried out in the absence of any inert liquid diluent.

7. A process according to any of claims 1 to 4 or 6 in which the titanium compound is from titanium trichloride.

8. A process according to any of claims 1 to 4, 6 or 7 in which the activated anhydrous halide support is used in admixture with an

anhydrous compound of an element of Group 45  
 III or IV of the Periodic System.

9. A process according to any of claims 1 to 5 in which the titanium compound is reacted with an electron-donor compound to form an addition compound, and the addition  
 50 compound is added to the carrier.

10. A process according to any of claims 1 to 5 or 9 in which the electron-donor compound is N,N',N'',N''' - tetramethylethylenediamine, dimethoxy-ethane, diethylene  
 55 glycol - di - methylether, tetrahydrofuran, or dioxan.

11. A process according to any of claims 1 to 5, 9 or 10 in which the titanium compound is titanium tetrachloride.

12. A process according to any of claims 1 to 5 or 9 to 11 in which the activated anhydrous halide support is used in admixture with an anhydrous compound of a metal  
 60 of Group I or II of the Periodic System.

13. A process according to any of claims 1 to 5 or 9 to 12 in which the polymerization is effected in an aliphatic, aromatic or cycloaliphatic hydrocarbon medium.

14. A process according to any of the preceding claims in which the titanium compound is present on the carrier to the extent  
 70 of from 1% to 10% by weight with respect to the carrier.

15. A process according to any of the preceding claims in which the molar ratio of hydride or organometallic compound to titanium compound is from 50 to 1000.

16. A process for the preparation of a polymer as described in any of the Examples.

17. A polymer prepared by a process according to any of the preceding claims.

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